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13. ABSTRACT (Maximum 200 Words)

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This material exhibits large second order nonlinear optical (NLO) effects subsequent to poling. In a poled film sample, second harmonic generation coefficient, d_{33}, of 34 pm/V was observed at 1.06 μm. Crosslinking is brought about by exposure to UV radiation at 254 nm wavelength. In a poled and crosslinked film sample, a d_{33} of 22 pm/V was observed. This d_{33} value is less than the d_{33} value of the poled and uncrosslinked film sample due to photo-induced cis-trans isomerization and partial degradation of the NLO chromophores. Nevertheless, the poled and crosslinked film shows a much more stable second order response at ambient conditions compared to the poled film which has not been crosslinked.

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UV Curable Epoxy-Based Second Order Nonlinear Optical Materials; Synthesis and Characterization

by

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UV-CURABLE EPOXY BASED SECOND ORDER NONLINEAR OPTICAL MATERIAL

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ABSTRACT

Epoxy based material incorporating 4-(4'-nitrophenylazo) phenylamine has been synthesized and subsequently functionalized with cinnamoyl groups. These materials can be easily solution-processed into thin films by spin-coating. The uncrosslinked polymer has excellent thermal and linear optical properties. Glass transition temperature of 115°C and degradation temperature (air) of 278°C were recorded.

This material exhibits large second order nonlinear optical (NLO) effects subsequent to poling. In a poled film sample, second harmonic generation coefficient, d_{33}, of 34 pm/V was observed at 1.06 μm. Crosslinking is brought about by exposure to UV radiation at 254 nm wavelength. In a poled and crosslinked film sample, a d_{33} of 22 pm/V was observed. This d_{33} value is less than the d_{33} value of the poled and uncrosslinked film sample due to photo-induced cis-trans isomerization and partial degradation of the NLO chromophores. Nevertheless, the poled and crosslinked film shows a much more stable second order response at ambient conditions compared to the poled film which has not been crosslinked.

INTRODUCTION

In general, organic molecules bearing electron donor and acceptor groups separated by a conjugated bridge have been shown to possess large values of nonlinear molecular hyperpolarizability [1]. The nonlinear optical (NLO) properties of such molecules dispersed in an amorphous polymer host have been examined by our research group [2] and other researchers [3, 4]. However, guest/host systems suffer from limited solubility of the NLO molecule in the polymer host, and orientation in amorphous polymer matrices is gradually lost over a period of time even at room temperature, the poled system being thermodynamically unstable.

A number of new homo- and copolymers bearing NLO-active molecules on the side-chain have been successfully synthesized [5]. The side-chain polymers exhibit improved stability of the NLO properties and a higher density of NLO moieties compared to guest/host systems. Much greater stability of NLO properties in a poled system was obtained from crosslinked polymers [6, 7].

Recently, a new class of photo-crosslinked system similar to a guest-host system was reported by our group[8]. The guest NLO molecule and the host polymer were both functionalized with photoreactive groups. In this system the sample can be poled and subsequently photo-crosslinked. A material with stable NLO properties is thus obtained. However, guest-host systems suffer from limited solubility of the NLO molecule in the polymer host. More recently, we reported a different approach for obtaining a crosslinked polymeric system with a higher molar concentration of NLO moieties by photochemical reaction [9]. This approach is based on the intermolecular photocrosslinking reactions of a NLO active polymer functionalized with photoreactive groups (figure 1). The photo-crosslinking reaction can be performed at a wavelength based on the absorption profile of the photoreactive groups which are pendant to the polymer main chains.

Since the second order susceptibility is directly proportional to the concentration of the NLO moieties and the temporal stability is dependent on the mobility of the NLO moieties in the polymer matrix, large and stable NLO properties are expected from these photo-crosslinked polymers. We report our investigations on one of these new photo-crosslinking systems based

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on the epoxy of the Diglycidyl Ether of Bisphenol A and 4(4'-nitrophenylazo) phenylamine (Disperse Orange 3) functionalized with cinnamoyl groups. Upon UV irradiation, the photoreactive epoxy polymers lead to a crosslinked network. We report on the stability at room temperature of the second order nonlinearity of the crosslinked and uncrosslinked polymer films. The linear and second-order nonlinear optical properties of poled polymer with or without crosslinking were measured at 1.06 microns and are reported uncorrected for absorption.
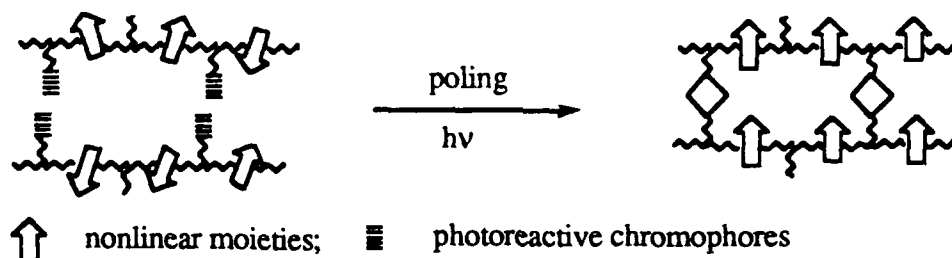

Figure 1. Schematic for the preparation of stable second order nonlinear optical polymers

EXPERIMENTAL

(a) Materials

Chemical synthesis of photoreactive epoxy polymer of Diglycidyl Ether of Bisphenol A and 4(4'-nitrophenylazo) phenylamine (Disperse Orange 3)(DGEBA-DO3C) is described in reference 10. The chemical structure of the polymeric product functionalized with cinnamoyl groups is illustrated in figure 2.
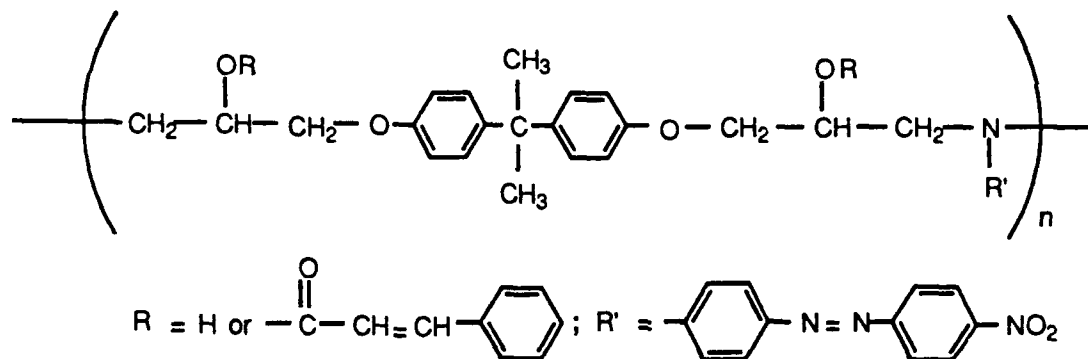

Figure 2. The structure of DGEBA-DO3C

DGEBA-DO3C was dissolved in propylene glycol methyl ether acetate and 1,4 dioxane (volume ratio 3:1) with a weight ratio of 1:10. The solution was spin-coated on glass and quartz slides, and KBr plates, respectively, and then baked at 70°C under vacuum for 12 hours. Typical film thickness obtained was approximately 0.66 μm. Indices of refraction at 532 nm and 1000 nm were measured using an ellipsometer.

(b) Methods

The glass transition temperatures, T_g, of the polymers are determined from differential scanning calorimetry (Dupont DSC2910) at a heating rate of 10K/min. The thermal decomposition temperatures (T_d) of the polymers were determined on a Dupont TGA2950 with a heating rate of 10K/min.

For UV irradiation, each sample was placed at a right angle to a Dymax optical fiber guided Mercury Lamp (main emission at 254 nm, cut off at 400 nm) at a specified distance and irradiated for 10 minutes.

UV/Vis spectra were recorded on a Perkin Elmer Lambda 9 spectrophotometer. Infrared spectra were recorded on a Mattson FTIR.

The poling technique used was corona poling in the wire to plane and in, in-situ needle

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poling arrangements[3, 5]. The poling temperature was set at 10°C below the glass transition temperature (T_g) of the uncrosslinked polymer. The second order nonlinear optical coefficient (d_{33}) of the poled thin film has been measured by second harmonic generation (SHG) from 1.06 micron laser radiation. The relaxation behavior of the second order nonlinear optical properties was studied by the decay of second harmonic (SH) intensity as a function of time after poling. The details of the experimental set-up have been reported elsewhere [2].

RESULTS AND DISCUSSION

Thermal Properties: Thermal properties of the uncrosslinked polymers are listed in Table I. The glass transition temperature (T_g) and the degradation temperature (T_d) increase after functionalization of hydroxyl groups. The content of functionalization was measured by the acetyl chloride titration method [11].

Table I. Thermal properties of polymers

	T_g(°C)	T_d(°C)[a]
epoxy prepolymer	105	237
DGEBA-DO3C[b] (76.5% functionalization of hydroxyl groups)	115	278

[a] in air.
[b] NLO density is 38 wt%.

Optimization of Radiation Dose: Photo-crosslinking of the NLO materials results in better temporal stability of the second order NLO properties. However, it also causes photo-induced cis-trans isomerization of the azo units and degradation of the NLO chromophores, which leads to the reduction of second order NLO activity [12]. Since there is a trade-off between stability, second order NLO activity caused by photo-crosslinking and photo-induced degradation, the optimum radiation dose has to be determined in a systematic manner. Table II illustrates the effects of UV radiation dose on SH intensity of DGEBA-DO3C studied by in-situ poling. When the incident UV intensity is 3 mW/cm^2, the SH intensity drops to 51% of its initial value

Table II. The effects of UV radiation dose on SH intensity of DGEBA-DO3C

UV Intensity (t = 10 min.)	Retention of SH Intensity*
3 mW/cm^2	51%
6 mW/cm^2	7%
12 mW/cm^2	0%

* monitored by in-situ poling.

after 10 minutes of UV irradiation. After 10 minutes of UV irradiation at an intensity of 12 mW/cm^2, the SH intensity was almost zero. On the other hand, when the UV intensity is less than 3 mW/cm^2, there is little photo-crosslinking reaction occurring after 10 minutes of UV irradiation as determined by IR and UV/Vis study. Based on the above, a dose of 3 mW/cm^2 for 10 minutes was chosen as optimal condition for UV irradiation for this polymer.

IR and UV/Vis Study of the Photo-chemical Reactions: Upon UV irradiation, the

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DGEBA-DO3C undergoes reactions that can be analyzed by IR and UV/Vis spectroscopy. As shown in figure 3, after 10 minutes of UV irradiation at 3 mW/cm^2, the carbonyl absorption peak at 1714 cm^{-1} becomes slightly broader and the C=C absorption peak at 1635 cm^{-1} decreases slightly. This indicates that a certain extent of photo-crosslinking has occurred. When the incident intensity is 12 mW/cm^2, dramatic photo-chemical reactions are seen as shown in figure 4. The carbonyl absorption peak at 1714 cm^{-1} shifts to 1730 cm^{-1} after 10 minutes of UV irradiation. This suggests that a significant portion of the conjugated carbonyl groups are now non-conjugated. In addition, the C=C absorption peak at 1635 cm^{-1} completely disappeared after exposure. The absorption peak corresponding to the nitro symmetric stretching at 1340 cm^{-1} also decreases sharply after UV irradiation. This is indicative of the degradation of the NLO dye and is detrimental in obtaining large second order nonlinearity.
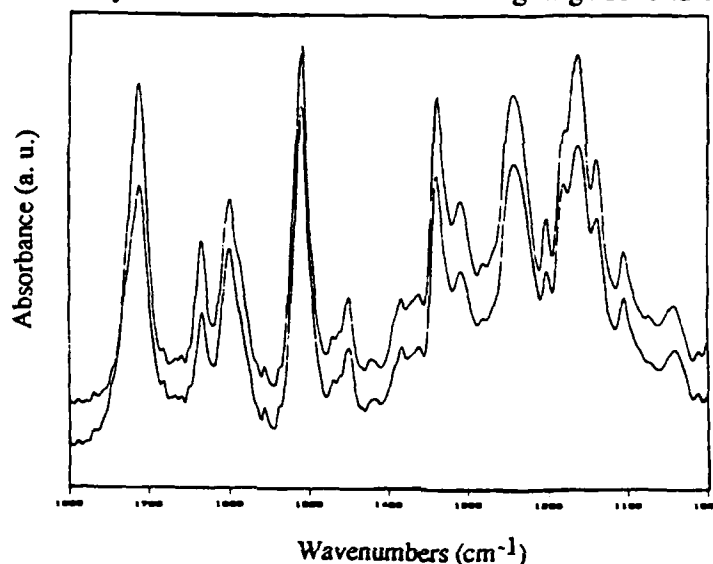

Wavenumbers (cm^{-1})

Figure 3. IR spectra of DGEBA-DO3C, before and after UV irradiation mainly at λ= 254 nm (I= 3 mW/cm^2) for 10 minutes in the presence of air. From top to bottom: before, after.

Wavenumbers (cm^{-1})
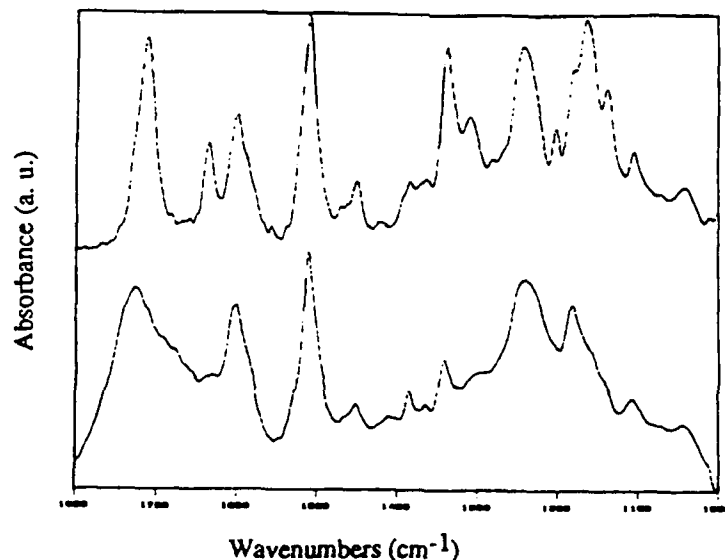
Figure 4. IR spectra of DGEBA-DO3C, before and after UV irradiation mainly at λ= 254 nm (I= 12 mW/cm^2) for 10 minutes in the presence of air. From top to bottom: before, after.

UV/Vis spectra of the uncrosslinked and crosslinked films are given in figure 5. After 10 minutes of UV irradiation (I=3 mW/cm^2), not only did photo-crosslinking occur (the absorption peak of 278 nm decreases), but photo-induced cis-trans isomerization and degradation of the NLO chromophores were also taking place simultaneously. This is indicated by the decrease in the intensity of absorption at 461 nm and increase around 370 nm.
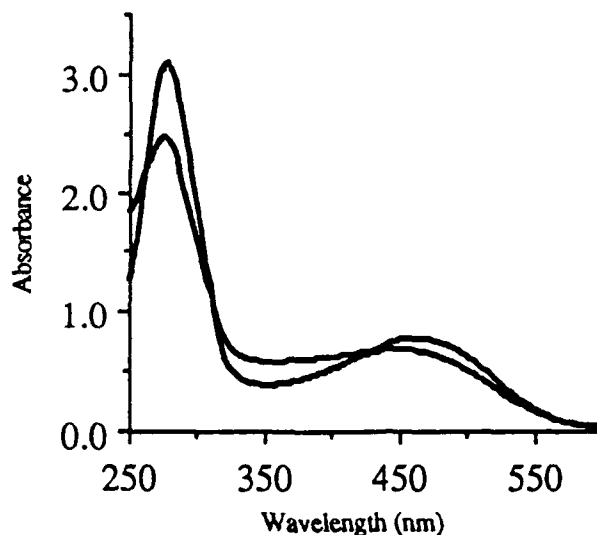
Figure 5. UV/Vis absorption spectra of DGEBA-DO3C before and after UV irradiation, mainly at $\lambda=254$ nm ($I=3$ mW/cm^2), for 10 minutes in the presence of air. From top to bottom (at $\lambda=278$ nm) : before, after.

Linear and Nonlinear Optical Properties: The second order NLO properties of DGEBA-DO3C have been characterized by second harmonic generation. The d_{33} values obtained for 1064 nm fundamental wavelength are listed in Table III along with some linear optical properties. This poled film sample has a d_{33} value of 34 pm/V without exposure to UV irradiation. A reduction of 35% in d_{33} was observed for the poled sample after 10 minutes of UV exposure. The d_{33} value of the poled and crosslinked sample is 22 pm/V.

The temporal stability of the SH intensity after poling and crosslinking have been observed with DGEBA-DO3C (figure 6). The result clearly indicates that the poled and crosslinked sample shows significantly improved stability. The uncrosslinked poled sample shows slow decay in SH intensity with time.

Table III. Optical properties of DGEBA-DO3C

Thickness (μm)	0.66
Abs. max. (nm)	461
Refractive indice	
λ (μm)	
0.532	1.718
1.000	1.652
d_{33} (pm/V)[a] at 1.06 μm	34
d_{33} (pm/V)[a] at 1.06 μm with UV irradiation	22

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[a] d_{33} not corrected for absorption.

In conclusion, epoxy-based materials containing disperse orange 3 as the NLO dye with reasonably large dye density and UV crosslinkable groups have been synthesized. This material upon poling exhibits large second-order NLO properties. The photo-crosslinked polymeric thin films showed a much more stable second order response compared to the uncrosslinked films in spite of photo-induced cis-trans isomerization and degradation of the NLO chromophores.
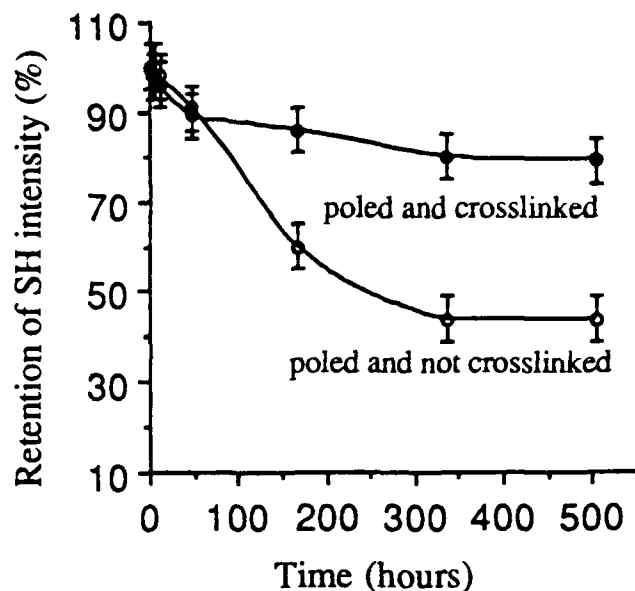
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Figure 6. Temporal behavior of second harmonic intensity of DGEBA-DO3C

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REFERENCES

1. D. Li, J. Yang, C. Ye, M. Ratner, G. Wong, and T. Marks, in Nonlinear Optical and Electroactive Polymers, Edited by P. Prasad and D. Ulrich, (Plenum Press, New York, 1988), p. 217.
2. B. Mandal, Y. Chen, R. Jeng, T. Takahashi, J. Huang, J. Kumar and S. Tripathy, Eur. Polym. J., 27, 735 (1991).
3. M. A. Mortazavi, A. Knoesen, S. T. Kowell, B. G. Higgins and A. Dienes, J. Opt. Soc. Am. B6, 733 (1989).
4 H. L. Hampsch, J. Yang, G. K. Wong, and J. M. Torkelson, Macromolecules, 23, 3640 (1990).
5. M. Eich, A. Sen, H. Looser, G. Bjorklund, J. Wwalen, R. Twieg, and D. Yoon, J. Appl. Phys. 66, 2559 (1989).
6. M. Eich, B. Reck, D. Y. Yoon, C. G. Willson and G. C. Bjorklund, J. Appl. Phys. 66, 3241 (1989).
7. J. W. Wu, J. F. Valley, S. Ermer, E. S. Brinkley, J. T. Kenney, G. F. Lipscomb, and R. Lytel, Appl. Phys. Lett., 58, 225, (1991).
8. B. Mandal, J. Kumar, J. Huang, and S. Tripathy, Makromol. Chem., Rapid Commun. 12, 63 (1991).
9. B. Mandal, J. Kumar, and S. Tripathy, PROC. Materials Research Society (MRS), Pittsburgh, 61 (1990).
10. B. Mandal, R. Jeng, J. Kumar, and S. Tripathy, Makromol. Chem. Rapid Commun. to be published.
11. H. Lee, and K. Neville, Handbook of Epoxy Resins, (McGraw-Hill Book Co., New York, 1967), p. 4-22.
12. M. Chen, L. Yu, L. Dalton, Y. Shi, and W. Steier, Macromolecules 24, 5421 (1991).

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